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INVESTIGATIONS ON SOME ALKALI HALIDES IN THE VACUUM ULTRAVIOLET

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WORK in the vacuum u.v. region of the spectrum has had a long tradition at Cornell. During the late twenties and early thirties it was largely devoted to investigations of the energy states of multiply ionized atoms and into the deeper energy levels of atomic systems, work which is today still continued in the research of Tombouljian and his students. Use of the spectral region as a tool in studying aspects of the solid state is more recent but is an obvious outgrowth of techniques and instruments developed for the other work. Some of this latter work may be said to have started with the investigations of SABINE⁽¹⁾ into the reflectivity in the vacuum u.v. of evaporated metal films of many metals. Subsequently, FERGUSON⁽²⁾ studied photoconductivity in NaCl and deduced an energy level scheme for the crystal from his results. The present program is an outgrowth that has come from an attempt to repeat his work.

In spite of considerable effort, photoconductivity in NaCl or any other alkali halide has not been seen by us, although in the past year groups at Rochester⁽³⁾ and in Japan⁽⁴⁾ have reported it. The fact that it appears to be of such small magnitude as to make its detection so difficult is in itself an interesting result. Beyond this, however, various aspects of the optical properties of alkali halides, properties of some of the centers occurring in them as revealed both by absorption and luminescent properties, and some photoemission properties have been studied and reported. This paper will attempt to review some of this and will include some recent results that have not yet been published.

Our monochromators are essentially Eagle mountings of concave gratings. Slits and grating rulings are horizontal and the entrance and exit slits, which are fixed, are displaced on opposite sides of the plane of the Rowland circle, such that the source and the detector chamber, wherein the physics is done, are situated side by side at one end of the vacuum enclosure. To scan the spectrum at the exit slit, the grating is of course tipped about the horizontal axis. These are blazed 1 m replicas of Bausch and Lomb As first used, no provision was provided for changing the grating focus. Later the modification of JOHNSON⁽⁵⁾ was incorporated wherein the grating is swung about a horizontal axis above it, achieving focus at two wavelengths.

More recently we have devised and built two instruments in which focus is achieved at all wavelengths. This incorporates a rather nice linkage and has proved to be so satisfactory that it warrants brief description here.* It turns out to be essentially a system

*Detailed description is presently in preparation for publication.

described by DOWELL.⁽⁶⁾ The geometry is indicated in Fig. 1. One imagines the two slits to be coincident with the pivot on one end of a rigid link connecting them to the center of the Rowland circle where the other end connects with another rigid link in a pivot, this link being rigidly connected and normal to the grating. The latter is confined to translational motion along a straight line through the slits. As the center of the Rowland circle is swung about a circle of its own radius, having the slits as center, the grating is

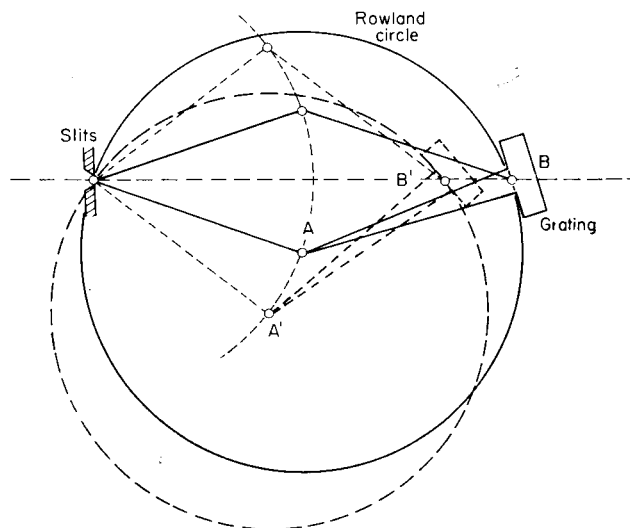


FIG. 1. Geometry of grating mounting.

moved forward and tipped accordingly such that both it and the slits always have the correct aspect to put on the exit slit focussed diffracted light from the entrance slit. To achieve a practical instrument one displaces the slits on opposite sides of the Rowland circle plane and develops the linkage somewhat further. Since we use it in the vertical plane, another identical link is coupled through gears to the first to put the linkage into static equilibrium, the grating now being coupled through another gear to the linkage as indicated in Fig. 2. Drive is achieved by loading an arm fixed to the grating cell such that it rides against a flat surface raised and lowered by a roller riding on a wedge which is driven in straight line motion from the outside. The reason for this somewhat complex drive is that we wanted to arrange two such monochromators in tandem to make possible a double monochromator for the elimination of scattered light. To provide a single control for two gratings, the above arrangement was devised. Although the two instruments are now mounted adjacently on piers such that in principle one can be swung over fairly easily to bolt onto the other, we have not actually tried the double pass combination. By the time they were built there appeared to be enough work for two instruments. Furthermore, various other means of obviating scattered light have been and are being devised. However, we believe that a double instrument is quite feasible with the source and detection system we use down to about 1000 Å.

Our sources have all been hydrogen capillary discharges⁽⁷⁾ which evolved from the early high voltage sources until they are now something of a hybrid between them and the

low voltage source described by JOHNSON⁽⁸⁾. Aside from the short quartz capillary and the metal-glass lead-in seals, the lamp is all metal. It has been reproduced in a number of places and appears quite satisfactory for much work in this region. While it is usually used with hydrogen, it works equally well with argon and nitrogen, which provides lines to about 800 Å. Using it with helium makes possible measurements at the resonance line at 584 Å. However, there is still need for a continuously operating source giving a copious line spectrum between 1000 Å and 500 Å.

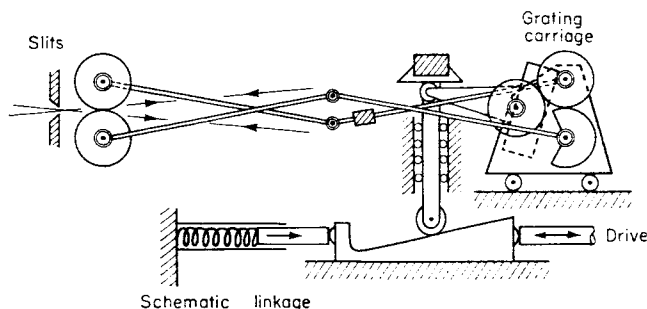


FIG. 2. Linkage used in focussing monochromator. The two links are not in the same plane to avoid an interference in crossing each other.

As detector of radiation we have used the usual luminescence of sodium salycilate and photomultipliers, recently the EMI 6097S. For some work other phosphors have been used where flatness of response is of not great moment. The photoemission from gold has been used with current detection by vibrating reed electrometer. For detection at longer wavelengths, the emission from copper iodide⁽⁹⁾ and silver iodide have been utilized.

In some work, as, for example, the determination of photothresholds, the presence of scattered light is always a serious consideration. Besides the double monochromator development, various other techniques, undoubtedly common to other workers in the field, have been employed to minimize it. We have used filters of various cutoff frequencies to provide discrimination between the wanted radiation and scattered radiation. Photoemission as a detector is rather useful over some regions in discriminating between the two, since the emission process is insensitive to radiation longer than a certain threshold—in gold this is around 1300 Å. Another system which shows promise is currently being worked on, evolving from the "hill and valley" technique with a line source as a means of discriminating against scattered light. This system is to make use of a line source to illuminate an entrance slit oscillating normal to its length, such that the wanted radiation from the exit slit is modulated while the scattered radiation is very largely not. Use will be made of a.c. tuned amplification and synchronous detection. No quantitative results can as yet be reported although the components are all nearly ready to put to trial.

The optical absorptions of the alkali halides are very high—in the order of 10^6 cm^{-1} . It is thus practically impossible to measure absorptions in anything but thin evaporated films. One of the earlier measurements we did⁽¹⁰⁾ was to repeat work of SCHNEIDER and O'BRYAN⁽¹¹⁾, but making use of phosphor-photomultiplier detectors instead of photography. This was done on NaCl and KCl, the crystals of our primary early interest,

this phosphor in the position of the first phosphor, in principle making for a nearly direct measurement of reflectivity. The rotatable light pipe of SMITH⁽¹⁴⁾ is, however, a more elegant solution to the problem of monitoring both reflected and incident light with the same detector.

Absorption measurements have been made by evaporating the material on thin films of Zapon which can be moved in and out of the path to the phosphor which converts the light for the multiplier. In some instances the evaporation has been onto a crystal of LiF, which enables cooling the film but which does limit measurement to wavelengths above 1050 Å. In one or two instances the film has been evaporated directly onto the phosphor. For example, in an unpublished measurement on solid argon absorption, NELSON deposited the phosphor on a block which in the measurement is cooled by liquid He and the argon is condensed directly onto this. Incident light was converted with another identical phosphor, light from both phosphors being collected by a hemisphere directing it to the photomultiplier. Lamp hydrogen was kept from diffusing into the cold chamber by a thin Zapon window seal slid in and clamped down over the exit slit of the monochromator after evacuation. The laying down of the investigated material on a rough phosphor such as sodium salicylate gives one pause as to what kind of microscopic geometry he is looking at. For such purposes, TIMUSK has tried evaporating the phosphor "luminogen" (2,2' Dihydroxy-1, 1' naphthalazine) which goes down more as a glassy surface on which one has more confidence in depositing his material to be studied. The response of this phosphor is not as high as that of sodium salicylate, however.

As indicated, a considerable effort has gone into the photoconductivity search in NaCl and KCl without success on our part. This has been coupled with an investigation on the external photoemission with which it is rather closely associated. The problem of detecting the true photoconductivity is very difficult. The presence of copious external emission gives rise to strong signals which are easily mistaken for photoconductive signals, this external emission being from the crystal under investigation itself or induced in the detector circuit by emission from various other surfaces in the vicinity which do see the radiation used. In measurements on the external emission both thin films and bulk crystals have been utilized with no essential difference in results. When bulk crystal is studied, means must be provided for discharging the surface following an irradiation and emission.

In the photoconductivity work various geometries, electrode arrangements and procedures were tried without success. One promising attack had interesting results, however. It was proposed that the surface of the crystal with electrodes laid down on it be overcoated with an evaporated layer of LiF which has its absorption edge far below that of the KCl and would thus be no emitter of electrons itself, in a region where one might expect the KCl to photoconduct. It turned out that LiF, in contrast to other alkali halides, had a long tail extending into the KCl edge region where photoemission was observed. Some recent work by LLOYD (not yet completed) shows this to not be intrinsic to the LiF, but an effect of the surface which grows with time, after either cleaving or evaporation. Beyond the tail is the sharp rise in the photoelectric yield typical of the other halides. The relative absorption he finds for LiF is indicated in Fig. 3 with the NaCl curves.

The very small magnitude of any photoconductivity in these materials we believe is associated with their extremely high absorptions. Any electron-hole pairs created must

in the emission process and found a surprising lack of sensitivity, with a few interesting exceptions.

While the interest in the photoconductivity problems remains and instrumentation is being attempted at extending and making easily reached higher energy regions of the spectrum, work recently has shifted somewhat to mixed systems of alkali halides and to luminescent centers induced by u.v. radiation. MAHR⁽¹⁷⁾ has investigated the absorption of the system KCl-KBr both in thin films and as single crystals, (in the latter case looking primarily in the variation of the edge of the fundamental absorption) as a function of relative concentrations. He observes absorption peaks of both components in strengths proportional to their concentrations and finds a concentration sensitivity in both the edge position as well as the absorption peak positions, which shift to higher energy as the KBr concentration increases, with the exception of the high energy KBr absorption peak which is almost independent of concentration. He interprets the results on the simple semiclassical basis that the absorbed photon transfers an electron from the halogen ion to the neighboring alkali ions, predictions from this model agreeing with the results quite well. The insensitivity of the high energy KBr peak is not well understood but may be caused by the electron going into an excited level or into exciton orbits of large radii. Figure 5 shows the variation in the absorption spectrum with concentration and Fig. 6 shows the position of the absorption maxima as functions of the lattice constant or, equivalently, the KBr mole percentage.

MAHR⁽¹⁸⁾ has more recently studied KCl with small concentrations of I⁻ added substitutionally. He finds two absorption bands in the transparent region of the KCl and in addition a luminescence excited by absorption of light in these two bands. He has determined the excitation and emission spectra for the process, as a function of exciting wavelength, temperature and concentration of iodine.

TIMUSK⁽¹⁹⁾, on the other hand, has investigated a luminescence occurring in pure alkali halides after pre-irradiation in their exciton absorption region, which presumably creates vacancies. He connects the sharp rise in its subsequent excitation spectrum with the position of the assumed photoconductivity step below the excitation absorption wavelength, mentioned previously, as the threshold wavelength where hole-electron pairs may be created. He ascribes the luminescence as due effectively to the capture of a hole by an *F*-center. Since the excited α center is essentially an exciton formed near a negative ion vacancy, the optical excitation corresponds to the excitation of an *F*-center in the field of a hole. He thus predicted the same emission when the crystal is irradiated in the alpha band itself. In fact this was found⁽²⁰⁾. On the basis that the onset of the emission is a manifestation of electron-hole pair creation (band-to-band transition) and utilizing various data for the photoelectric threshold, he arrives at the electron affinities for NaCl, KCl, KBr, and KI as 0.8, 0.6, 0.9, and 1.6 eV respectively, in fair agreement with what one expects from calculation. Figure 7 shows the excitation spectra he observed in the four crystals. The sharp rise is the assumed band-to-band transition threshold and the minima occur at absorption maxima to support TEEGARDEN's⁽²¹⁾ supposition that they arise because the absorption is then so close to the surface that radiationless recombination takes place. Our notion that photoconductivity is similarly inhibited by high absorption at the surface fits this picture.

In conclusion I should emphasize, although it should be obvious, that most of the work reported here is not my own. I wish to express my pleasure at being associated

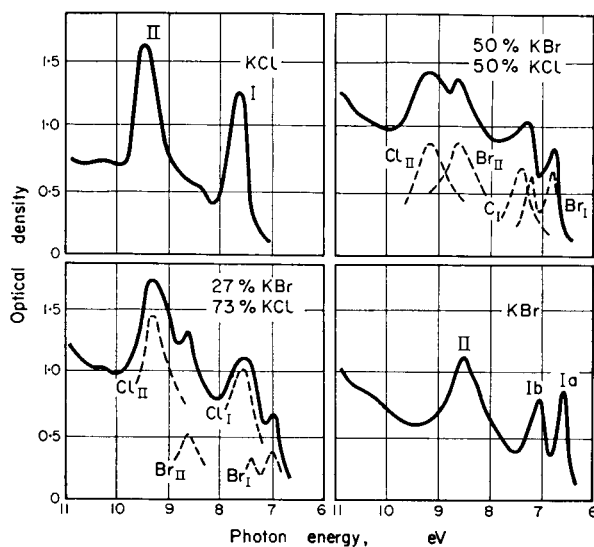


FIG. 5. Absorption spectra of the mixed system KCl-KBr at four concentrations. The dotted curves indicates the locations and amplitude of peaks needed to synthesize the result, from which shifts in peak positions for Fig. 6 are obtained

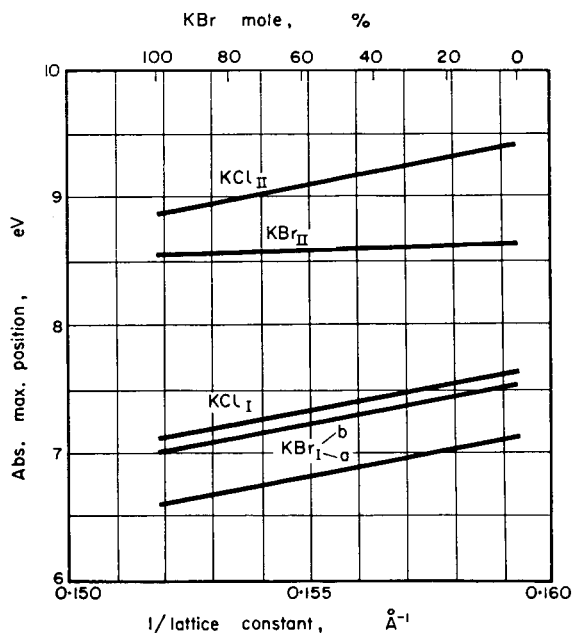


FIG. 6. Shift in absorption peak positions in the KCl-KBr system as functions of KBr concentration or lattice constant.

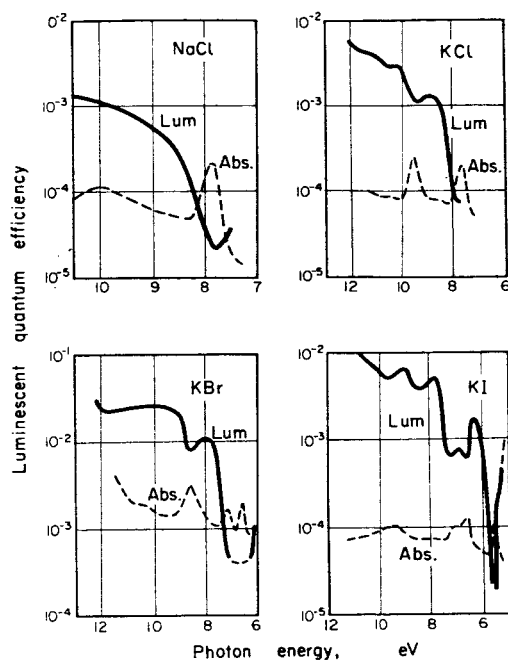


FIG. 7. Excitation spectra for luminescence of four alkali halides after pre-irradiation in the exciton band.

with the people whose work it is and in being able to take some small part in it with them here and there, and to express my appreciation to them for allowing me to include it in this summary.

It is also a privilege to acknowledge our indebtedness to the U.S. Office of Naval Research which has supported this work in a very large measure.

REFERENCES

1. G. B. SABINE, *Phys. Rev.* **55**, 1064 (1939).
2. J. N. FERGUSON, Jr., *Phys. Rev.* **66**, 220 (1944).
3. Y. NAKAI and K. J. TEEGARDEN, *Int. Photoconduct. Conf.* to be published (1961).
4. G. KUWABARA and K. AOYAGI, *Int. Photoconduct. Conf.* to be published (1961).
5. P. D. JOHNSON, *Rev. Sci. Instr.* **28**, 833 (1957).
6. J. H. DOWELL, *J. Sci. Instr.* **17**, 208 (1940).
7. P. L. HARTMAN and J. R. NELSON, *J. Opt. Soc. Amer.* **47**, 646 (1957).
8. P. D. JOHNSON, *J. Opt. Soc. Amer.* **42**, 278 (1952).
9. C. RACZ, *J. Chim. Phys.*, **39**, 175 (1942).
10. P. L. HARTMAN, J. R. NELSON, J. G. SIGFRIED, *Phys. Rev.* **105**, 129 (1957).
11. E. G. SCHNEIDER and H. M. O'BRYAN, *Phys. Rev.* **51**, 293 (1937).
12. E. A. TAFT and H. R. PHILLIP, *J. Phys. Chem. Solids*, **3**, 1 (1957); *Phys. Rev.*, **106**, 671 (1957).
13. J. E. EBY, K. J. TEEGARDEN, D. B. DUTTON, *Phys. Res.* **116**, 1099 (1960).
14. A. SMITH, *J. Opt. Soc. Amer.*, **50**, 862 (1960).
15. J. W. TAYLOR and P. L. HARTMAN, *Phys. Rev.* **113**, 1421 (1959).
16. L. APKER, E. TAFT and J. DICKEY, *J. Opt. Soc. Amer.* **43**, 78 (1953).
17. H. MAHR, *Phys. Rev.* **122**, 1464 (1961).
18. H. MAHR, *Bull. Amer. Phys. Soc.* **7**, 178 (1962); *Phys. Rev.* **125**, 1510 (1962).
19. T. TIMUSK, *J. Phys. Chem. Solids*, **18**, 265 (1961).
20. T. TIMUSK, *Bull. Amer. Phys. Soc.* **7**, 38 (1962).
21. K. J. TEEGARDEN, *Phys. Rev.* **105**, 1222 (1957).